

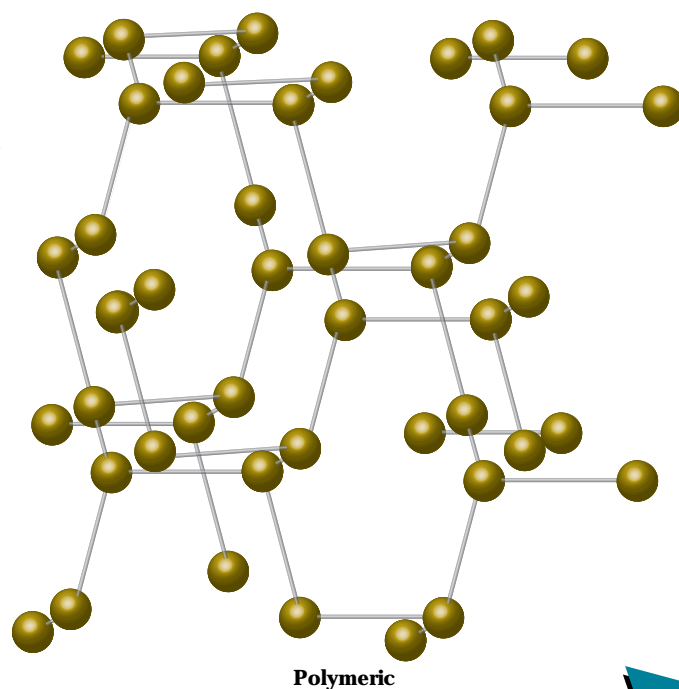
Polymeric Nitrogen: A Potential Compound to Store Energy

R ESEARCHERS throughout the industrialized world are looking for alternative sources of energy to relieve the world's heavy reliance on fossil fuels. Fossil fuels are not only polluting, but they will eventually be depleted if consumed at current rates. In addition, the political realities of the post-Cold War era place renewed emphasis on the performance of conventional weapons, which could be enhanced by the creation of more energetic explosives.

One potential compound that can store energy is nitrogen, which makes up 78% of the atmosphere. Each atmospheric nitrogen atom naturally combines with another to form N_2 , a diatomic molecule held together with the strongest bond known—a triple covalent bond. Theory suggests that if a volume of N_2 is sufficiently squeezed, the nitrogen will give up its diatomic structure and form a continuous network of single covalent bonds. This polymeric structure is like that observed in its chemically similar neighbor, phosphorus. At normal atmospheric pressure and temperature, polymeric nitrogen should be a highly energetic metastable solid.

Our first-principles, quantum-mechanical calculations indicate that 1 cm^3 of polymeric nitrogen would store 34 kJ of energy—an amount virtually identical to that of diesel oil and gasoline and nearly three times that of HMX, one of the more powerful explosives in the world. Moreover, the energy released when polymeric nitrogen returns to the diatomic state would be pollution free: the sole reaction product would be environmentally benign N_2 gas.

Having only covalent bonds, polymeric nitrogen differs from most conventional liquid and solid fuels, propellants, and explosives (e.g., gasoline, liquid H_2/O_2 mixtures, and HMX). These other energy sources have covalent bonds within each molecule that alternate with extremely weak van der Waals interactions between the molecules.



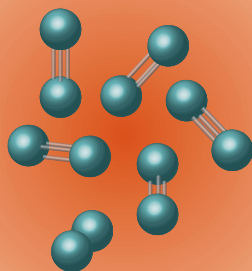
Polymeric nitrogen therefore packs a larger number of atoms in a given volume and can store a correspondingly larger amount of energy per unit of volume than other sources.

A decade-long history of theory and experiment in high-pressure physics has revealed trends across the periodic table of the elements. One such trend suggests that applying pressure to an elemental solid will cause it to assume the structure and bonding of a heavier element in the same column of the table at atmospheric pressure. For example, the stable phase of carbon at 1 atm is graphite, which transforms under pressure to the diamond structure. Diamonds, which are metastable solids at 1 atm, have the same structure as silicon and germanium at 1 atm.

Theory has played an important role in examining this trend. At pressures up to ~100 GPa (100 GPa = 1 Mbar = 1 million atm), some 44 phases have been encountered for the elemental solids in groups III, IV, and V of the periodic table. Well over half of these phases have been investigated theoretically, and phase identification has shown near perfect agreement with experiment.

We have predicted that, in the absence of energy barriers, nitrogen should always be diatomic below 65 GPa and polymeric above this pressure. However, energy barriers retard the effect of increased pressure and are typically quite large between two covalent phases. Therefore, the diatomic-to-polymeric transition in nitrogen should occur

*The hoped-for payoff:
polymeric nitrogen
returning to the stable
diatomic form, with a
large release of energy.*



Diatomic

at a much higher pressure than 65 GPa. For example, even when carbon is heated to 1000 K, the graphite-to-diamond transition requires roughly a factor of seven times more pressure than that predicted without energy barriers. Although energy barriers will make the synthesis of polymeric nitrogen at high pressure more difficult, they will help stabilize the polymeric phase once synthesized.

Our calculations suggest that the reverse transition (polymeric-to-diatomic) should also occur at a much lower pressure than 65 GPa—at least for a polymeric solid without defects or free surfaces. We are currently enhancing our present theoretical capabilities to determine the impact of defects and of room-temperature atomic vibrations on the metastable lifetime of polymeric nitrogen at 1 atm.

Current Research

To synthesize polymeric nitrogen, we are using one of LLNL's diamond anvil cells, a robust device with a small (~20 μm diameter) sample chamber within which pressures exceeding that at the center of the earth (~350 GPa or 3.5 Mbar) have been reached. Nitrogen at room temperature has retained its diatomic form in the diamond anvil cell up to pressures of 180 GPa. By contrast, analysis of shock-wave data imply that nitrogen

becomes a fluid of single atoms at ~6000 K and at the relatively low pressure of 30 GPa. (In shock compression, a supersonic pressure wave hitting the sample induces brief conditions of high pressure and temperature.) However, laser heating in a diamond anvil cell allows more controlled access to the extremes of pressure and temperature than does shock compression.

We therefore plan to heat the sample by transmitting an intense laser beam through one of the transparent diamond windows. We have already achieved 2000 to 6000 K temperatures in the diamond anvil cell. This combination of high temperature and pressures, or “hot isostatic pressing,” is a tried and true materials processing technique, although so far only at pressures of tens of GPa. Our technique will extend this range in pressure by more than an order of magnitude.

To diagnose our nitrogen sample, we will use Raman scattering. When a laser beam is transmitted through the diamond anvils onto the sample, some of its photons are scattered by lattice vibrations in the nitrogen solid, leading to measurable frequency shifts in components of the beam. Raman scattering is an *in situ*, real-time diagnostic that allows us to see directly the strong triple bond that we hope to break. This diagnostic will immediately indicate the synthesis of polymeric nitrogen by the disappearance of the triple bond and the appearance of new vibrational modes.

We have begun our laser-heating efforts in the 100 GPa regime and have obtained clear indications of pressure-induced weakening of the triple N_2 bond. We are now using larger samples with a more powerful laser to minimize heat loss to the diamond anvils. With recent experimental improvements, we are confident that we can achieve ~5000 K in our high-pressure N_2 samples. After we synthesize a small sample of polymeric nitrogen at high pressure and demonstrate its stability at atmospheric pressure, production scale-up by other means will be explored.

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